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CONDUCTIVITY OF DILUTE GADOLINIUM NITRATE AND NITRIC ACID SOLUTIONS IN D_2O AND H_2O AT 25°C

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ABSTRACT

Electrical conductivities of <0.001M solutions of $Gd(NO_3)_3$ and HNO_3 in D_2O and H_2O were determined at 25°C. Limiting equivalent conductances ($\Lambda°$) were calculated by the Onsager limiting law and the Shedlovsky equation. The $\Lambda°$ values in H_2O agreed within 1% with those estimated from the literature. Conductivities of non-stoichiometric (nitrate-rich and nitrate-deficient) gadolinium nitrate systems were also measured.

INTRODUCTION

Because of the high neutron absorption cross section of some of its isotopes, gadolinium can be used to control nuclear reactivity. Injection of gadolinium nitrate solution into the D_2O coolant-moderator of the Savannah River Plant (SRP) reactors provides a supplementary mode of reactor shutdown [1]. The concentration of dissolved gadolinium during subsequent cleanup of the D_2O by ion exchange is indicated by in-line conductivity measurements.

Interpretation of measured conductivities in terms of solute concentrations depends on (1) the availability of experimental conductivity data for dilute solutions, and (2) prior characterization of the chemical behavior of $Gd(NO_3)_3$ in the coolant-moderator. Suitable conductivity data for dilute electrolyte solutions and for solutions in D_2O were not available in the literature. Conductivities of gadolinium nitrate in H_2O at concentrations >0.003M have been reported [2]. Conductivity measurements of 0.0002 to 0.1M gadolinium chloride solutions [3] are the basis for the limiting equivalent conductance value of the gadolinium ion [4].

However, the concentration of gadolinium cannot be determined by conductivity measurements alone in nonstoichiometric gadolinium nitrate solutions that contain excess nitric acid or gadolinium hydroxide. Nitrate-deficient solutions are produced by contact with the hydroxyl form of the deionizer ion-exchange resin, which selectively removes nitrate from the solution. Such solutions tend to precipitate $(Gd(OH)_3$.

As part of a study of the chemical behavior of $Gd(NO_3)_3$ in an SRP reactor system [5], the conductivity of nitric acid and gadolinium nitrate at concentrations less than 0.001M in H_2O and D_2O was measured. Limiting equivalent conductances were calculated for the nitric acid and gadolinium nitrate systems. Commercial apparatus was used that could later be adapted for off-line analyses of process samples, if required.

EXPERIMENTAL

Apparatus

Conductivity was measured with a Model RC-19 conductivity bridge (Beckman Instruments, Inc.), which has a stated accuracy of ±0.25% of the reading. Measurements were made at a frequency of 100 Hz. The bridge was balanced with respect to both resistance and capacitance. Supplemental capacitance was furnished by external decade capacitance units. A capacitance of $\sim$0.7 µF was required for the more concentrated (0.001M) solutions. This caused a readout error only slightly greater than 0.25% [6].

The conductivity cell was a Beckman Model CEL-K01 dip-type cell. The cell constant was certified by the manufacturer to be 0.100 cm^{-1} ± 0.25%. The cell was attached to a 50-mL glass container by a rubber sleeve so that the cell could be withdrawn from or inserted into the solution without opening the system. The container was equipped with ports for addition of N_2 and electrolyte solution.

- 3 -

The system was maintained at 25 ± 0.05°C in a constant-temperature water bath. At the time of each conductivity reading, the temperature was verified by a certified thermometer (Sargent Welch) next to the glass container.

Reagents

The D_2O and H_2O were purified by passing them through columns of Amberlite® MB-1 mixed ion-exchange resin (Rohm and Haas Co.). Triply distilled H_2O, purified for radiolysis experiments, was also used. Density measurements demonstrated the isotopic purity of the D_2O to be greater than 98 vol %. The background conductivity of these solvents was between 0.3 and 0.7 μmho/cm.

The HNO_3 was ULTREX (J. T. Baker Co.) ultrapure quality. Stoichiometry of the $Gd(NO_3)_3$ was ensured by adding gadolinium oxide (99.9%, Atomergics Chemetals Co.) to a concentrated solution of gadolinium nitrate (99.9%, Alfa Products) and titrating with dilute HNO_3 [7].

Nitrate-rich solutions were prepared by combining gadolinium nitrate and nitric acid. Nitrate-deficient solutions were prepared by selective removal of nitrate from gadolinium nitrate solutions by anion exchange [5].

Procedure

Fifty milliliters of solvent (H_2O or D_2O) was equilibrated under a stream of nitrogen at 25 ± 0.05°C until the conductivity was constant (about 30 minutes).

Increments of 0.1M solute [Gd(NO$_3$)$_3$ or HNO$_3$] in H$_2$O or D$_2$O were then added from a micropipet. The conductivity was measured after each addition, by alternately withdrawing and inserting the conductivity cell into the stirred solution until successive measurements yielded a constant conductivity. The nitrogen purge of the gas space was continued throughout the measurements.

The final solute concentrations were determined by titration. Intermediate concentrations were calculated. Gadolinium ion was titrated in hexamethylenetetramine hydrochloride buffer at pH 5.5, with 0.01M Na$_2$H$_2$EDTA* and xylenol orange indicator [8]. Hydrogen ion was titrated to pH 7 with 0.01N NaOH. A blank correction to the titration was necessary for each solvent. The effective concentration of the NaOH for titration of these dilute solutions was determined by titration of 100-μL portions of 0.1M HCl, previously standardized with tris-(hydroxymethyl)aminomethane (NBS Standard Reference Material) [9].

Supplementary measurements with KCl and HCl solutions [10] demonstrated the validity of the analytical techniques and the conductivity measurements and verified the value of the cell constant.

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* G. Frederick Smith Chemical Company "Primary Standard"; EDTA = ethylenediamine tetraacetic acid.

Calculations

The equivalent conductance (Λ, in mho-cm^2 per equivalent) of each solution was calculated from

$$\Lambda = 0.001 \ (G-G_O)/Mz \tag{1}$$

where

    G = specific conductance, or conductivity, of solution, μmho/cm

       = (cell constant) x (bridge reading with solution)

    G_O = specific conductance, or conductivity, of solvent, μmho/cm

       = (cell constant) x (bridge reading with solvent)

    M = concentration of solute [HNO_3 or $Gd(NO_3)_3$] in solution, moles/liter

    z = number of equivalents/mole of solute

       = 1 for HNO_3

       = 3 for $Gd(NO_3)_3$

Limiting equivalent conductances, Λ°, were derived by extrapolation of the experimental data to infinite dilution ($M \to 0$) by two standard methods [4]. The first uses the Onsager limiting law, which is applicable to dilute solutions:

$$\Lambda^\circ = \Lambda + A\sqrt{M} \tag{2}$$

where A is a constant. The second method uses the equation of Shedlovsky:

$$\Lambda^{\circ\prime} = \frac{\Lambda + B_2 \ \sqrt{M}}{1 - B_1 \ \sqrt{M}} \tag{3}$$

The constants B_1 and B_2 are the relaxation term and the electrophoretic term, respectively, derived from the theory of con-

ductivity. Values are listed in Table 1. Tabulated values of B_1

and B_2 for the H_2O solutions were used [4]. Values for D_2O

solutions were calculated, using tabulated values for the viscosity

and dielectric constant of D_2O [11].

RESULTS AND DISCUSSION

Pure Solutes

The experimental data are presented in Table 2 as molar concen-

trations and equivalent conductances calculated with a cell con-

stant of 0.1002 cm^{-1}. The trend of the gadolinium nitrate data is

generally consistent, to higher equivalent conductance at lower

concentrations. The nitric acid data are less satisfactory,

showing considerable scatter. It should be recognized, however,

that the nitric acid solutions are three-fold less concentrated than

the gadolinium solutions in terms of electrical equivalents.

In Figures 1 through 4, the Onsager and Shedlovsky interpreta-

tions of the experimental data are compared for each solvent-solute

system. For the Onsager limiting law, Equation 2, a least-squares

straight line has been drawn through the equivalent conductance

data, to locate the intercept Λ°. For the Shedlovsky interpreta-

tion, Equation 3, a line is drawn through the average of the $\Lambda^{\circ\prime}$

values. The limiting equivalent conductances, Λ°, obtained by the

two methods, i.e., the intercepts at the ordinate, are nearly the

same.

Table 3 summarizes the limiting equivalent conductances
determined in this work and compares them with literature values.
The conductances obtained by summing limiting ionic conductances
are about 1% lower for gadolinium nitrate and 0.5% higher for
nitric acid than the values found in this work. The limiting
equivalent conductance of gadolinium nitrate in H_2O [12], estimated
from published data for 0.003 to 0.03M gadolinium nitrate solutions
[2], is also lower than the value determined in this work. The
value found for gadolinium nitrate in D_2O is higher than that
estimated from the literature data for H_2O using Walden's rule [4].**

In Table 4, the experimental values are examined for their
adherence to Walden's rule. Agreement between theoretical and
experimental values is good in the gadolinium nitrate system, re-
sembling values for other salts, potassium chloride and sodium
chloride. Deviations from the rule for the nitric acid system are
similar both in direction and magnitude to conductivity ratios
reported for nitric acid and hydrochloric acid.

Mixtures

Conductivities of nitrate-rich and nitrate-deficient [5] mix-
tures were measured to determine the effects of non-stoichiometry.
Measured and calculated conductivities are compared in Table 5.

** Walden's rule states that the product of the viscosity of the
    solvent and the limiting equivalent conductance is constant
    for a given solute.

At these low concentrations, the conductivities of gadolinium nitrate and nitric acid in the nitrate-rich system are nearly additive. The measured conductivity of a solution containing both solutes at concentrations of 0.0003M was only about 1% lower than the sum of the measured conductivities of the individual 0.0003M solutions.

For nitrate-deficient solutions, the observed specific conductance is slightly lower than that calculated by assuming that all the soluble gadolinium*** is gadolinium nitrate. The calculated total conductivity based on total gadolinium is much higher than that observed.

The measured conductivity of solutions with various degrees of nitrate depletion is shown in Figure 5. The solutions contained about 0.001M total gadolinium, but were not visibly turbid. The conductivity is roughly proportional to the concentration of soluble gadolinium. The slope of the straight line provides an estimate of the effective equivalent conductance of gadolinium nitrate in this system: about 122 mho-cm^2 per equivalent in H_2O and about 102 mho-cm^2 per equivalent in D_2O. These equivalent conductances are similar to those of stoichiometric 0.001M gadolinium nitrate.

*** Soluble gadolinium is defined as gadolinium not retained by filtration through a 0.45-micron Millipore® (Millipore Corporation) filter.

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LIST OF TABLES

LIST OF FIGURES

Table 1

Solute	Solvent	B_1	B_2
$Gd(NO_3)_3$	H_2O	1.3259	297.12[†]
$Gd(NO_3)_3$	D_2O	1.3272	240.55
HNO_3	H_2O	0.2300	60.65[†]
DNO_3	D_2O	0.2302	49.10

[†]Ref.[5].

Table 2

$Gd(NO_3)_3$ in H_2O		$Gd(NO_3)_3$ in D_2O		HNO_3 in H_2O		HNO_3 in D_2O	
M[††]	Λ[§]	M[††]	Λ[§]	M[††]	Λ[§]	M[††]	Λ[§]
9.525	125.3	10.33	102.5	11.86	412.9	12.91	305.1
9.465	126.4	10.11	103.1	9.906	414.5	12.84	305.4
9.426	125.6	9.161	103.3	9.781	413.1	11.77	304.6
9.261	125.5	9.114	103.3	9.712	414.1	10.83	302.3
7.612	126.8	6.857	104.8	7.941	414.7	10.72	304.6
5.756	128.5	6.805	104.7	7.832	414.9	10.71	304.3
4.635	129.4	4.650	107.1	7.777	414.2	10.78	304.6
3.814	131.2	4.644	106.7	5.967	416.3	9.816	305.6
2.343	133.5	2.327	109.3	5.880	414.9	8.685	303.7
1.916	133.6	2.325	109.3	5.839	414.7	8.642	305.8
1.165	134.4	1.154	111.2	3.924	417.0	8.595	305.8
0.977	135.5	1.150	111.1	3.896	416.9	8.588	304.4
				1.964	415.4	7.861	304.9
						6.527	303.4
						6.494	306.2
						6.459	306.2
						6.454	304.9
						5.901	304.7
						4.360	304.3
						4.338	307.5
						4.315	307.8
						4.311	305.6
						3.938	305.1

[†] Cell constant = 0.1002 cm^{-1}.
[††] Concentration is $M \times 10^{-4}$ moles/liter.
[§] Λ is equivalent conductance, mho-cm^2/equivalent.

Table 3

| Solute | Solvent | Limiting Equivalent Conductance, mho-cm^2/equivalent, by | | | |
		Onsager Equation 2[†]	Shedlovsky Equation 3[†]	Sum of Ionic Conductances[††]	Estimated From Literature[§]
Gd(NO$_3$)$_3$	H$_2$O	140.0 ± 0.5	140.3 ± 0.5	138.76	137.0 ± 0.2
Gd(NO$_3$)$_3$	D$_2$O	115.4 ± 0.2	115.3 ± 0.3	–	112.7 ± 1.3[§§]
HNO$_3$	H$_2$O	419.2 ± 0.8	419.0 ± 0.8	421.26	–
DNO$_3$	D$_2$O	307.7 ± 1.1	308.4 ± 1.1	–	–

[†] Indicated precision measure is standard deviation.
[††] Ref. 5
[§] Ref. 3,12
[§§] Walden's rule (Ref. 5).

Table 4

System	Temperature, °C	$\Lambda^{\circ}_{H_2O}/\Lambda^{\circ}_{D_2O} = \eta_{D_2O}/\eta_{H_2O}$	Reference
Theoretical	25	1.232	11
$Gd(NO_3)_3$	25	1.22	This work
$HNO_3(DNO_3)$	25	1.36	This work
Theoretical	18	1.256	11
KCl	18	1.2225	11
NaCl	18	1.2280	11
HCl(DCl)	18	1.3895	11
$HNO_3(DNO_3)$	18	1.3885	11

Table 5

Solute	Concentration in H_2O, molarity				Specific Conductance, μmho/cm	
	$Gd(NO_3)_3$	HNO_3	Total Gd	Soluble Gd	Observed	Calculated
$Gd(NO_3)_3$	0.0003	–	–	–	112.1	–
HNO_3	–	0.0003	–	–	120.6	–
$Gd(NO_3)_3$ + HNO_3 (nitrate-rich)	0.0003	0.0003	–	–	230.1	232.7
$Gd(NO_3)_3$ + $Gd(OH)_3$ (nitrate-deficient)	–	–	0.00058	0.00041	151	159(soluble Gd) 230(total Gd)
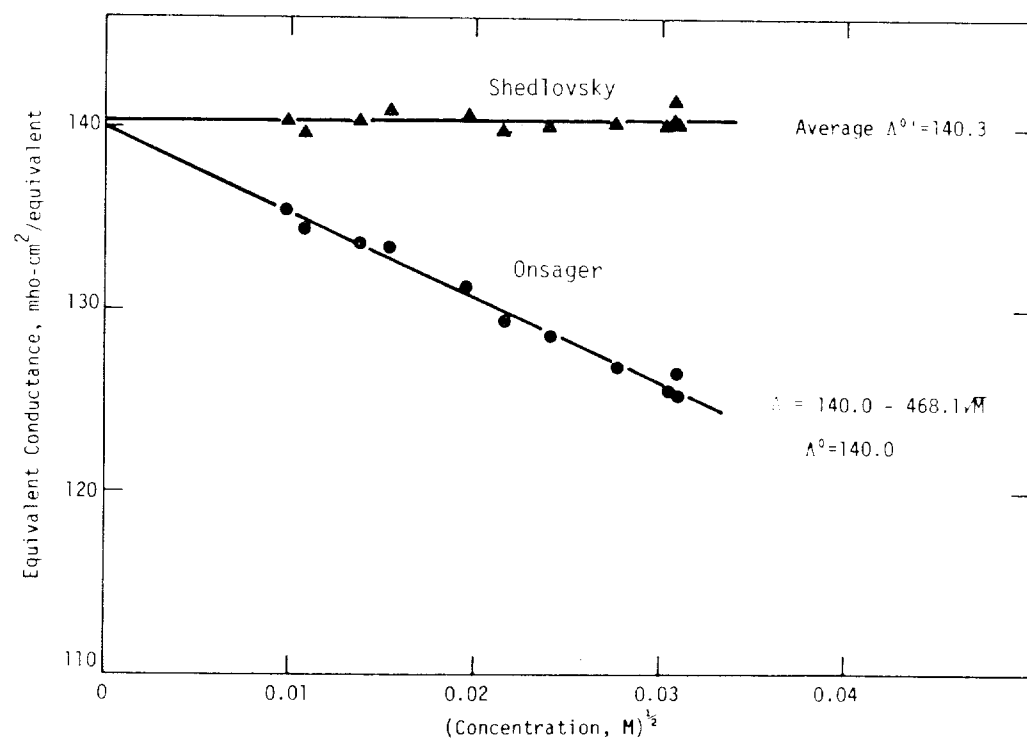
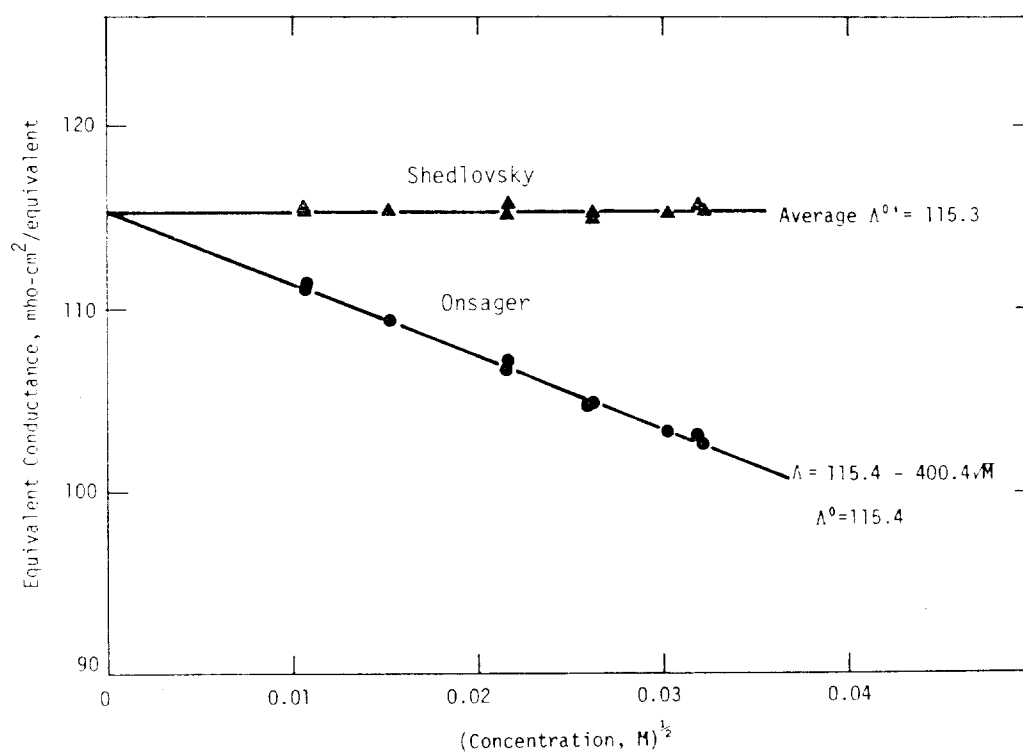Fig. 1. Equivalent conductance of $Gd(NO_3)_3$ in H_2O at 25°C

Fig. 2. Equivalent conductance of $Gd(NO_3)_3$ in D_2O at 25°C
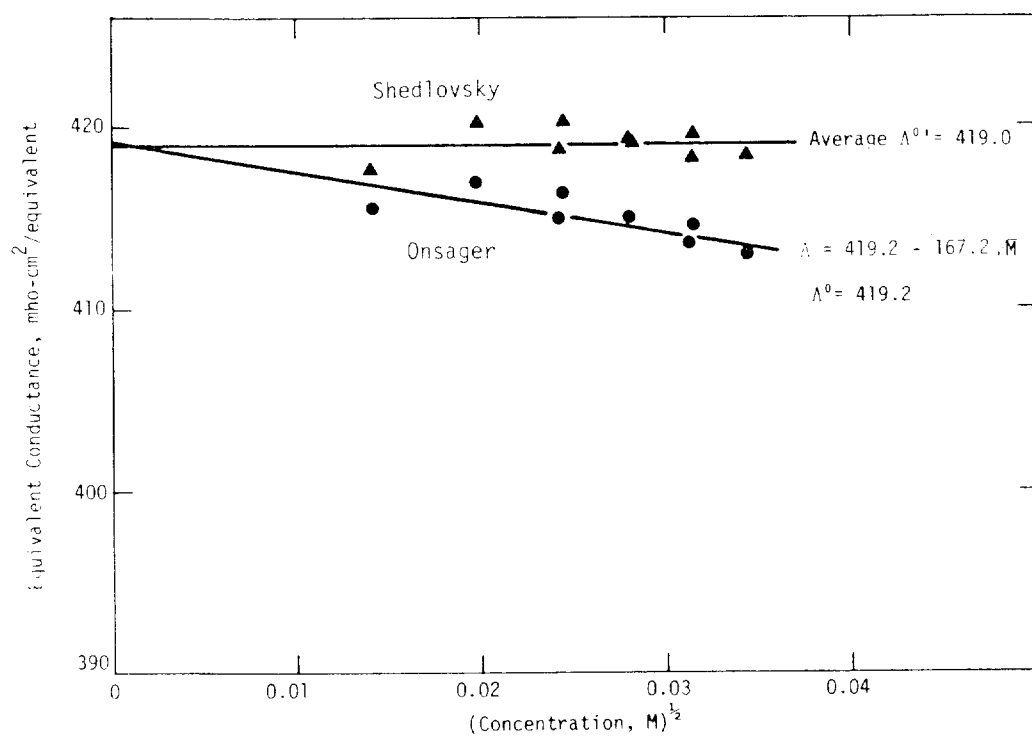
Fig. 3.   Equivalent conductance of HNO_3 in H_2O at 25°C
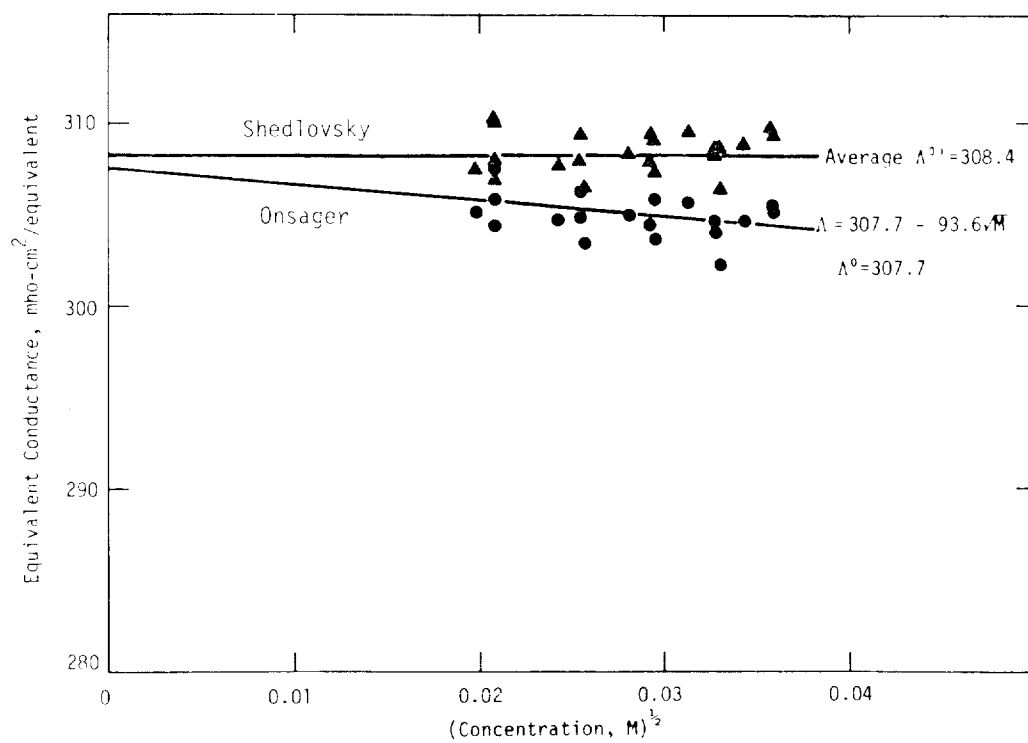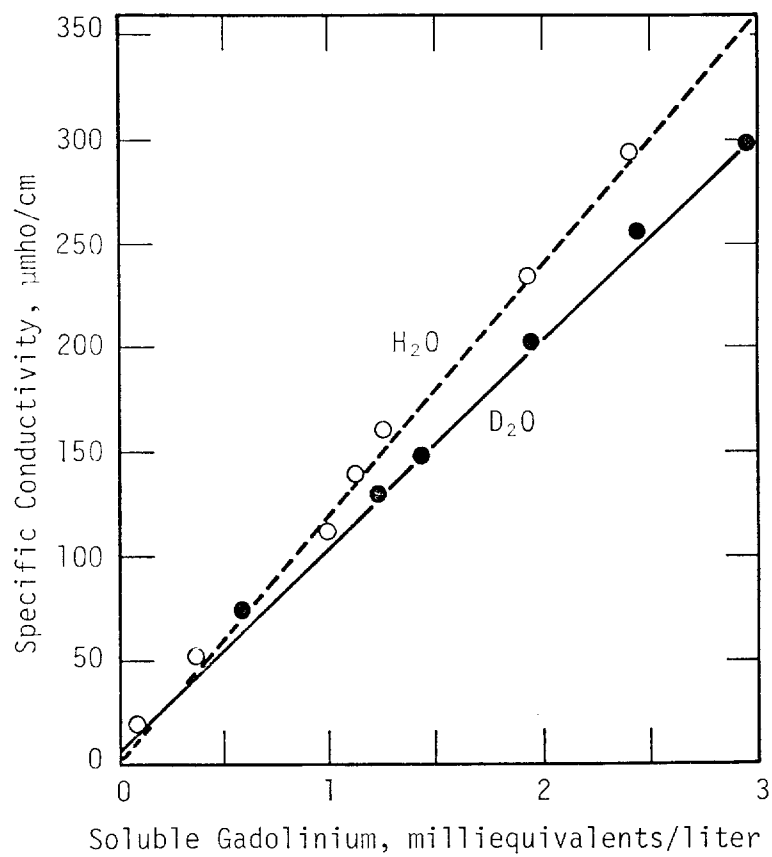
Fig. 4. Equivalent conductance of DNO_3 in D_2O at 25°C

Fig. 5. Relationship of conductivity and soluble gadolinium